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PATENT SPECIFICATION

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(19)

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(54) PESTICIDAL COMPOSITIONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pesticide formulations, and more especially to pesticides formulated in a particularly suitable form for rapid dispersion in water. In particular the invention relates to water-insoluble pesticides formulated as dispersible grains, and to a process for producing pesticide formulations in the form of dispersible grains.

One of the main problems which has existed in the pesticide industry has been that of formulating water-insoluble pesticides into convenient formulations which will rapidly form dispersions in water. Formulations in the form of dispersible powders are known but these are not particularly convenient to use and, in certain circumstances, can be hazardous, both in use and manufacture. Powdered formulations are bulky, and are not always easy and safe to pack. Consequently research into pesticide formulations has moved towards granular products, which, to some extent, avoid the disadvantages which are experienced with powders. Granular formulations are of particular value when the alternative of grinding to form a powdered formulation involves a material or substance which it is hazardous to treat in this way.

Numerous processes have been evolved for producing granules and these employ a variety of known techniques such as slurry- and spray-drying of a wet mix containing the pesticide and other ingredients. These processes, nonetheless, often involve grinding and/or pelleting techniques.

A particularly convenient, and relatively inexpensive, process has now been devised and is set out below. The process allows of the production of water-dispersible grains which are solid, free-flowing formulations, free of dust, rapidly wetting when added to water and dispersing therein at a high rate. The content of pesticide (active ingredient) can be high when required and the product has a high bulk density.

The invention provides a process for producing water-dispersible grains having a particle size within the range 0.5 to 5mm and comprising at least 15% by weight of a solid water-insoluble pesticide and at least 4% by weight of a dispersing agent, comprising forming an extrudable, aqueous mix from the water-insoluble pesticide, the dispersing agent and a disintegrating agent, the pesticide being substantially all in the form of particles less than 200 microns in diameter, extruding the mix to form moist coherent granules, drying the granules and recovering, if necessary by sieving, granules having a particle size within the range 0.5 to 5mm.

By the term 'water-insoluble' we mean having a solubility in water at 20°C of not more than 1% by weight.

Often, the pesticide to be formulated in the process is available in the form of a press paste, or filter cake, containing a proportion of water. It is preferred to include a wetting agent in the mix in addition to the dispersing agent. Any fillers used may also be incorporated in the mix, as well as any other ingredients, e.g., water-soluble pesticides, for example herbicidal bipyridylium salts.

The aqueous mix is conveniently mixed in a ribbon or similar type blender and a preferred form of extruder to carry out the extrusion step is one wherein there is provision for further mixing in the extruder head.

The free moisture content of the mix is adjusted so that the extruded mix emerges from the extruder in a crumbly form.

This adjustment, or selection, of the free moisture content is vital to the success of the process. If the mix is too wet, the extrudate emerges from the extrusion die as a

continuous column (like spaghetti), and does not break into granules of the desired size range. If the mix is too dry, the extrudate does not form coherent granules and breaks up into dust during the drying stage. If the mix is too dry, this may obviously be corrected by the addition of water or an aqueous solution. If too wet, it may be partially dried by conventional means, e.g., by gentle heating or vacuum treatment; or, preferably, by mixing with a water-deficient salt. After drying it may be necessary or desirable to sieve the grains to remove any fine material that may have been formed during the process.

In the context of this specification a dispersing agent is a surface active agent which facilitates the dispersion of the pesticide particles when the product is added to a liquid, for example water. The dispersing agents used are preferably water-soluble ones. Those which may be used, for example, include lignosulphonate salts, for example Polyfon H; condensation products of formaldehyde with a sulphonated unsubsituted or substituted phenol, aniline, or naphthalene or derivative thereof, and optionally with urea, examples of such condensation products being known by the names Dispersol T and Dyapol PT. "Dispersol" is a Registered Trade Mark.

A wetting agent is to be understood as a surface active agent which facilitates the wetting of the dispersible grains into water. Wetting agents which may be used in the process and formulations of the invention may include, for example, alkylated benzene sulphonate salts such as, for example Arylan S.B. and Arylan SX; ethylene oxide condensates with aliphatic alcohols, amines or acids or alkyl phenols, for example that known as Lissapol NX which utilises nonyl phenol; alkyl naphthalene sulphonates such as, for example Perminal BX. "Lissapol" and "Perminal" are Registered Trade Marks.

All surface-active agents (surfactants) act as dispersing agents in some degree, and also in some degree as wetting agents; most surface-active agents are however more efficient in one capacity than the other. The worker experienced in the formulation art can select a surfactant most suitable for the purpose in view.

A disintegrating agent in the present specification is intended to mean a solid, readily water-soluble substance, e.g., a salt or a simple organic substance, which aids the disintegration of the dispersible grains when these are added to water, to form a dispersion. By virtue of their ready solubility, or other reaction when brought into contact with the liquid, they assist in the breaking-up of the grains, Substances which may be used as disintegrating agents include the following: sodium acetate, sodium sulphate, sodium bicarbonate and citric acid. Mixtures of disintegrating agents are often conveniently used.

A water-deficient salt is defined as a salt which is capable of taking up water as water-of-crystallisation in order to reduce the quantity of free moisture present in the mix to the level where the mix itself has a satisfactory behaviour on extrusion. Suitable water-deficient salts include, for example, sodium actate, sodium sulphate and magnesium sulphate. If desired the same salt can be included in the mix for extrusion to serve both as a disintegrating agent and as a water-deficient salt; that is, it can perform a dual function.

The particle size of the pesticide used is lower than 200 microns. In general the preferred particle size is from 5 to 50 microns, but larger or smaller particle sizes are satisfactory, The press paste of the pesticide often contains, for example, between 10 and 50 per cent, by weight, of water.

In the present specification, by the term 'pesticides' we mean chemical crop protection agents, and include insecticides acaricides, molluscicides, herbicides, plant growth modifying agent, plant fungicides, plant bactericides and plant anti-viral agents. Specific pesticides which have been formulated into dispersible grain formulations according to the invention include those set out in the list below.

The invention is not to be considered as restricted to these specific pesticides, however, which are referred to merely by way of illustration only.

Common Name	Chemical Name
Captan	N - (trichloromethylthio)cyclohex - 4 - ene - 1,2 - dicarboximide.
Captafol	N - (1,1,2,2 - tetrachloroethylthio) - cyclohex - 4 - ene - 1,2 - dicarboximide.
Drazoxolon	4 - (2 - chlorophenylhydrazono) - 3 - methyl - 5 - isoxazolone.
Metazoxolon	4 - (3 - chlorophenylhydrazino - 3 - methyl - 5- isoxazolone.
Ethirimol	2 - ethylamino - 4 - methyl - 5 - *n* -butyl - 6 - hydroxyprimidine.
Pirimicarb	2 - dimethylamino - 5,6 - dimethyl-pyrimidin - 4 - yl dimethylcarbamate.
Simazine	2 - chloro - 4,6 - bis(ethylamino) - 1,3,5 - triazine.

Other water-insoluble pesticides which may be formulated by the process of this invention are listed in H. Martin's "Pesticide Manual" 3rd Edition, published by the British Crop Protection Council.

The free moisture content, or degree of wetness, of the extrudable aqueous mix is dependent upon a number of factors, including the nature of the particular pesticide used and the actual proportion of the mix constituted by it; the particle size of the pesticide; and the general rheological properties of the mix. In general, however, the free moisture content of the extrudable aqueous mix will lie between 5 and 25 per cent by weight.

The apparatus used to form the mix may be, for example, ribbon blenders or offset spiral mixers, such as, for example, those known by the names "Winkworth" and "Gardener". As an alternative a planetary auger mixer, such as, for example, that known by the name "Nauta" may be employed. "Nauta" is a Registered Trade Mark.

In general any extruder may be used to carry out the extrusion step of the invention process, particularly convenient extruders are those known by the name "Elanco". A particularly preferred extruder for small scale manufacture is the "Elanco" XDC 100 model. It is preferred that the extrusion orifices, that is the actual holes through which the mix is pressed and extruded, are constituted by screens having aperture sizes between 0.55 millimetres and 1.2 millimetres, although rather larger apertures may be used if desired. In operation the mix is supplied to the machine and fed by rotating feeding screws therein to an extruding chamber the walls of which are fitted with screens of the aperture size described. The rate of extrusion may vary within wide limits but in general on the Elanco XDC 100 a satisfactory rate is, for example, from 35 kilograms to 120 kilograms of extrudate pressed through the screens per hour.

The drying of the crumbly extrudate may be carried out using any type of drying apparatus. If necessary the extrudate can be dried by simply allowing it to stand but forced drying is quicker and more convenient. It is preferred to use a fluid-bed drier: a suitable fluid-bed drier is a "Manesty-Petrie" drier, type MP100S. Such drying is preferably carried out by raising the temperature of the extrudate: for example, to 60°C for half-an-hour (shorter times and higher temperatures could be used and vice versa).

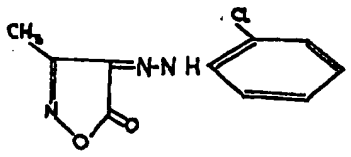
If sieving to remove fine material is necessary, any type of sieve of suitable mesh size may be used. The sieve is preferably vibrated by mechanical action. A convenient size of sieve is, for example, one having a British Standard mesh of between 8 and 30. A convenient method of operation is to sieve the extrudate through a mechanically vibrated BS 8 mesh sieve, discarding coarse grains remaining on the sieve, and thereafter sieving the grains which have passed through the sieve on a mechanically vibrated B.S. 30 mesh sieve, discarding grains and fines passing therethrough, and using, as the finished product, the grains remaining on the B.S. 30 mesh screen.

Discarded coarse and fine material can be recirculated and added to the next batch of mix for extrusion.

The invention is illustrated by the following examples.

EXAMPLE 1

This example illustrates the preparation of a dispersible grain formulation containing the pesticide having the British Standard Common Name of Drazoxolon. This substance is represented by the chemical formula:



and has the chemical name:— 4-(2-chlorophenylhydrazodo) - 3 - methyl - isoxazolone.

The ingredients used in the formulation are listed below, the name or trade name of each constituent being given together with an indication of its action and the proportion used or present. The formula given is to produce 10 kilograms of 60% drazoxolon dispersible grains. The drazoxolon had a particle size in the range 2.5 to 20 microns and was manufactured as an aqueous press paste (filter cake).

	Amount Used (Grams)
Drazoxolon aqueous press paste (71.8% active ingredient, 75.5% solids).	8360
Polyfon H (dispersing agent)	1500
Arylan SB (wetting agent)	100
Sodium bicarbonate	400
Anhydrous sodium acetate	372
G T Y Powder (china clay diluent)	1318

The ingredients are blended together in a "Nauta" mixer for ten minutes. The press paste is added first, then the sodium acetate and thereafter the other ingredients. The resultant damp powdery mix is extruded at approximately 90 kilograms per hour through an "Elanco" extruder (Model XDCS100) using a screen with 0.55 millimetre apertures.

The extrudate emerging from the screen breaks up into moist coherent granules. The product is collected and dried on a fluid bed drier with an inlet temperature of 60°C. to a residual water content of 3.5% when determined by the Dean & Stark method. The product is then sieved to obtain the fraction passing through a 10 mesh B.S. (British Standard) screen and collected on a 30 mesh B.S. screen (fines passing through the latter screen being rejected — fines and oversize grains can be recirculated in the next batch).

The product complied with the following specification:—

Disintegration and suspensibility

1.0 gms product added to 100 mls standard hard water "World Health Authority Specification for Pesticides" 2nd Edition, 1961 (WHO, Geneva) in a Crow receiver and the receiver inverted 15 times. The receiver is placed in a water bath at 30°C;

After 2 minutes, the amount of sediment should be no more than a trace.

After 5 minutes, the amount of sediment should not exceed 0.1 ml.

After 30 minutes, the amount of sediment should not exceed 0.3 mls.

After 30 minutes the suspension is passed through a 120 mesh B.S.S. (diameter 8.5 cms) and after washing with one litre water, there should be no material retained by the sieve.

Appearance:

Free flowing granular product.

Moisture Content:

Between 2.0 and 5.0% water by Dean and Stark.

Sieve analysis:

To pass 10 mesh B.S.S. but be retained on 30 mesh B.S.S.

EXAMPLE 2

This example illustrates the preparation of a 50 Kg batch of a dispersible grain formulation containing paraquat ion and simazine.

Paraquat concentrate (36.1% cation)	10.4 litres
Simazine (Technical grade)	15.0 kg
Cetyl trimethyl ammonium bromide	2.0 kg
Magnesium sulphate (anhydrous)	28.0 kg

The magnesium sulphate is charged into a mixer and the paraquat ion in the form of a strong solution of paraquat dichloride added thereto and mixed with it. The simazine (having a mean particle size of 5 microns) and surfactant are then added and mixed in.

The resultant mix is extruded, dried and sieved in the manner described in Example 1.

The product complied with the specification set out in Example 1.

EXAMPLE 3

This example describes the preparation of a dispersible grain formulation containing the pesticide known by the common name pirimicarb.

The formula for a 4 Kg batch is as follows:—

Pirimicarb (aqueous press paste, mean particle size 25 microns, 78% solids)	2.56 Kg
Dyapol P.T.	0.6 Kg
Sodium acetate (anhydrous)	0.4 Kg
Blue Lake dye	0.04 Kg
Talc S2	0.96 Kg

The ingredients are mixed together (active ingredient first followed by sodium acetate and then remaining ingredients) in a "Nauta" mixer, the final mix for extrusion containing 9.5% by weight free water.

The mix is then extruded, as before, (Example 1) at approximately 40 kilograms per hour. The product was dried in a fluid bed drier with an inlet temperature of 60°C until the residual moisture content is between 0.5 and 1%. It is then sieved between 8 and 30 B.S. mesh sieves the product retained being that passing through the 8 mesh sieve but held on the 30 mesh sieve.

The product complied with the specification set out at the end of Example 1 except that (a) 0.2 grams product were used in the disintegration and suspensibility test and the 5 and 30 minutes sediment limits were 0.05 ml and 0.1 ml respectively. (b) The moisture content of the product lay between 0.5 and 1%.

EXAMPLE 4

This example illustrates the preparation of a dispersible grain formulation containing Captan as the pesticide (active ingredient). The formula is as follows:

Captan (technical grade powder, mean particle size 5 microns)	2,500 g
"Polyfon" H	375 g
Sodium bicarbonate	875 g
"Arylan" SB	50 g
Sodium acetate (anhydrous)	205 g
Spestone	1,200 g
Water	1,000 g

Mixing of the above ingredients is carried out for 3 minutes in a ribbon blender. One litre of water was then added and mixing continued for a further five minutes.

The mixture, which contained 13.0% free water, was then extruded, dried and sieved as described in Example 1 above. The product

analysed at a captan content of 45.0% and contained no water. When added to water disintegration rapidly took place to form an aqueous suspension of the pesticide.

The following is a more detailed explanation of some of the constituents used in the formulations of the foregoing examples.

Dyapol PT (Sppiier, Yorkshire Dyeware) is believed to be a condensate of sulphanilic acid, formaldehyde and urea. It also contains sodium sulphate.

Talc S2 is a coarse grade of talc, viz, complex hydrated magnesium alumino silicate.

Polyfon H. (supplier, Westvaco, U.S.A.) is sodium lignin sulphonate.

Arylan S.B. (supplier Lankro Chemicals) is a branched chain dodecyl benzene sulphonic acids. Spectone is a fine grade of china clay.

Herbicidal grains containing mixtures of insoluble herbicides with herbicidal bipyridylium salts (e.g. halides) are particularly conveniently formulated according to this invention. Grains containing mixtures of paraquat and simazine are illustrated in Example 2. Similarly may be made grains containing mixtures of salts of diquat with the insoluble herbicide diuron; and grains containing mixtures of 1,1'-bis (N,N-diethylamino-carbonylmethyl) 4,4' bipyridylium salts with the insoluble herbicide atrazine.

As illustrated in the foregoing examples, the invention further consists in water-dispersible grains having a size within the range 0.5 to 5mm., comprising at least 15% and generally not more than 80% by weight of a solid water-insoluble pesticide in the form of particles less than 200 microns in diameter, a disintegrating agent, generally in amounts of from 5 to 60% by weight, and at least 4% but preferably not more than 25% by weight of a dispersing agent, having a water content (measured by the Dean and Stark method) of not more than 5%, and dispersing at a 1% dilution in standard hard water at 30°C to give substantially no sediment after two minutes.

WHAT WE CLAIM IS:—

1. A process for producing water-dispersible grains having a particle size within the range 0.5 to 5mm and comprising at least 15% by weight of a solid water-insoluble pesticide as defined herein and at least 4% by weight of a dispersing agent, comprising forming an extrudable aqueous mix from the water-insoluble pesticide the mix having a free moisture content as described herein, the dispersing agent and a disintegrating agent, as defined herein, in which the pesticide is substantially all in the form of particles less than 200 microns in diameter, extruding the mix to form moist coherent granules, drying the granules, and recovering the granules having a particle size within the range 0.5 to 5mm.

2. A process as claimed in claim 1, wherein the step of forming the extrudable aqueous mix includes the adjustment of the free moisture content of the mix by the addition of water.

3. A process as claimed in claim 1 in which the step of forming the extrudable aqueous mix includes the adjustment of the free moisture content by the addition of a water-deficient salt.

4. A process as claimed in claim 3 wherein the water-deficient salt is a disintegrating agent.

5. A process as claimed in either of claims 3 or 4 wherein the water-deficient salt is sodium acetate, sodium sulphate or magnesium sulphate.

6. A process as claimed in any of claims 1 to 5 wherein the mix is extruded through a screen having aperture sizes in the range 0.55 to 1.2 millimetres.

7. A process as claimed in any of claims 1 to 5 wherein the granules are dried in a fluid bed drier.

8. A process as claimed in any of claims 1 to 7 wherein a water-soluble pesticide is added during formation of the extrudable aqueous mix.

9. A process as claimed in claim 8 wherein the water-soluble pesticide is a herbicidal bipyridylium salt.

10. A process as claimed in any of claims 1 to 9 wherein both a wetting agent and a dispersing agent are added in forming the extrudable aqueous mix.

11. A process as claimed in any of claims 1 to 10 wherein the water-insoluble pesticide is a fungicide.

12. A process as claimed in any of claims 1 to 10 wherein the water-insoluble pesticide is an insecticide.

13. A process as claimed in claim 1, wherein the step of recovering the granules includes sieving of the dried granules.

14. Processes for preparing water dispersible grains substantially as described in any of Examples 1 to 4 herein.

15. Water-dispersible grains prepared by a process claimed in any of claims 1 to 14.

16. Water-dispersible grains having a size within the range 0.5 to 5mm, comprising at least 15% by weight of a solid water-insoluble pesticide, as defined herein, in the form of particles less than 200 microns, in diameter, a disintegrating agent, as defined herein, and at least 4% by weight of a dispersing agent, a water content (measured by the Dean and Stark method) of not more than 5%, and dispersing at a 1% dilution in standard hard water at 30°C to give substantially no sediment after two minutes.

17. Grains claimed in either of claims 15 or 16 which comprise from 15 to 80% by weight of water-insoluble pesticide.

18. Grains claimed in either of claims 16

or 17 which comprise from 4 to 25% by weight of dispersing agent.

19. Grains claimed in any of claims 16 to 18 which comprise from 5 to 60% by weight of disintegrating agent.

20. Grains as claimed in any of claims 16 to 19 wherein the water-soluble pesticide is a fungicide.

21. Grains as claimed in any of claims 16 to 19 wherein the water-insoluble pesticide is an insecticide.

22. Grains as claimed in claim 20 wherein the water-insoluble pesticide is drazoxolon.

23. Grains as claimed in claim 20 wherein the water-insoluble pesticide is metazoxolon.

24. Grains as claimed in claim 20 wherein the water-insoluble pesticide is captan.

25. Grains as claimed in claim 21 wherein the water-insoluble pesticide is pirimicarb.

26. Grains as claimed in any of claims 15 to 19 which additionally contain a water-soluble herbicidal bipyridylium salt.

27. Grains as claimed in claim 26 wherein the water-insoluble pesticide is simazine and the bipyridylium salt is a paraquat salt.

28. Grains as claimed in claim 26 wherein the water-insoluble pesticide is diuron and the dipyridylium salt is a diquat salt.

29. Grains as claimed in claim 26 wherein the water-insoluble pesticide is atrazine and the bipyridylium salt is a salt of the 1,1'-bis (N,N - dimethylaminocarbonylmethyl)4,4'-bipyridylium ion.

30. Water-dispersible grains substantially as described in any of Examples 1 to 4.

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